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<p>(21) International Application Number: PCT/PL92/00002</p> <p>(22) International Filing Date: 28 January 1992 (28.01.92)</p> <p>(30) Priority data: P 289.906 16 April 1991 (16.04.91) PL</p> <p>(71)(72) Applicants and Inventors: MYSŁOWSKI, Włodzimierz [PL/PL]; ul. Skalna 16, 43-309 Bielsko-Biala (PL). NIESCIEROWICZ, Aleksander [PL/PL]; ul. Browarna 27/14, 43-300 Bielsko-Biala (PL).</p> <p>(74) Agent: LUKASZYK, Maria; ul. Wróblewskiego 51A/10, 41-103 Siemianowice (PL).</p>		<p>(81) Designated States: AT (European patent), AU, BE (European patent), CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), HU, IT (European patent), JP, KR, LU (European patent), MC (European patent), NL (European patent), NO, RU, SE (European patent), US.</p> <p>Published <i>With international search report.</i></p>
<p>(54) Title: FIREPROOF MATERIAL</p> <p>(57) Abstract</p> <p>The fireproof material consisting of the carrier and the material increasing its volume under the influence of temperature, having water glass in its composition and in which, according to this invention, the most advantageous carrier are the granules of foamed polystyrene or ground foamed polystyrene with the granules of 0,5 to 20 mm in the quantity of 85 to 94 per cent by volume surrounded by the swelling agent in the quantity of 6 to 15 per cent by volume and consisting of water glass in the quantity of 65 to 85 per cent, advantageously colloidal silica in the quantity of 2 to 35 per cent, hydrophobizer in the quantity of 0.5 to 5 per cent and the colouring mineral pigment in the quantity of 0.1 to 1.8 per cent and hiding inorganic pigment in the quantity of 0.2 to 2 per cent. The fireproof material can be used for filling the doors and fire walls, for filling niches and spaces in the constructions with a special fire resistance, for shaping fire-proof plates, for building culverts, fire dams etc.</p>		

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FIREPROOF MATERIAL

Technical field

The subject of the invention is fire-proof material destined for filling the doors and fire-proof building walls, filling the niche room in the construction of special fire resistance, forming the fire-proof plates, building the culverts and fire dama etc.

State of technique

The known fire-proof agents are chemical compounds serving mainly for making the flammable materials more fire-resistant so that they can meet the requirements for the non-inflammable materials. The fire-proof agents are the mixtures of different chemical compounds appearing in the form of solutions, paints or varnishes. Depending on the kind of components contained therein they show fire-proof behaviour whose basis are physical or physical and chemical processes. There exist fire-proof agents which swell under the influence of heat and form a foamy substance as well as the agents which melt under the influence of heat and cover the material in this way with a tight coating, they secure it make it fire-proof from the inside because they penetrate deeply into the material. There exist also the fire-proof plates among which those made from keramsite and phenol coated with glass mat show the best fire-resistance. Improvement of fire-resistance of many well known laminated elements with polyurethane, phenol or polyester core has been achieved through introducing fibre glass into the core or by using inorganic middle layers between the inside and the metal layers.

From the certifikate of the Polisch Institute of Building Technique No 601/86 which allows swelling silicate coatings to be used in building engineering we know dam coatings consisting of two layers.

In this coatings it is possible to find the core consisting of the mixture of sodium and potassium silicates with the addition of plstificators, filling materials and porophors

where the carrier of the mixture is a non-woven made from non -alkaline glass glued with synthetic resin. The outer layer of the coating is formed by a layer of transparent varnish put on the core from both sides. In the high temperature the barrier coatings are swelling and form a slightly porous foam with melting point above 900 degrees centigrade surrounded by a layer of carbonized varnish. The known barrier coatings, as soon as they are glued on the surface of a flammable wood-like material such as chipboard, softboard, hardboard or aplywood, form a kind of fire protection.

According to Polisch standart PN-64/B-02850 dealing with fire-protection states six classes of fire-resistance for building materials.

The fire-resistance is expressed in the time /in hours/ in which the building element, in the case of fire, can fulfill the function required. In case of fire of a building, the doors are the elements of special importance.

There exist fire-proof doors worked out by the Centre of Design and Development of Industrial Building "BISTYP" in Warsaw, filled with isolating and fire-proof material, produced in the version of 0,5 and 1 hour of fire-resistance. This kind of door has the certificate allowing to use it in building technology No 33/88 issued by the Institute of Building Technique in Poland, however it cannot be used in housing. In order to fill the known fire-proof door, the basalt wool with density of 150 kg/m^3 is used. The layer of this wool 5 cm thich gives the fire-resistance of 0,5 hour.

Protection of a flammable material with the known fire-proof agents does not mean that the material is made non -flammable, but it only creates the conditions which brake the processes related with burning. Moreover, surface protection with fire-proof agents does not raise the class of fire-resistance of the element of the building. The effectiveness of pro-

tection of flammable materials with fire-proof agents known is differentiated and depends on the properties of protected materials. The same fire-proof agent put on two different materials can show up to be effective for one of them and not effective for the other.

Disclosure of the invention

The essence of this invention is to work out a recipe for fire-proof agent consisting of the carrier and the agent increasing its volume under the influence of temperature, having water-glass as its component, in which, according to the invention the most advantageous carrier are the granules of foamed polystyrene with the granules of 0,5 up to 20 mm in the quantity of 85 to 94 per cent by volume, surrounded by the swelling agent in the quantity of 6 to 15 per cent by volume, consisting of water -glass in the quantity of 65 to 85 per cent, advantageously colloidal silica in the quantity of 2 to 35 per cent, hydrophobizer in the quantity of 0,5 to 5 per cent and the colouring mineral pigment in the quantity of 0,1 to 1,8 per cent and hiding mineral pigment in the quantity of 0,2 to 2 per cent. Under high temperature, the fire-proof material shows a great fire-resistance while the thicker its layer is the greater its fire-resistance. The swelling substance increases its volume and the carrier from fomed polystyrene disappears when heating. The hollow room after the foamed polystyrene are being occupied by the swelling agent according to the principle of implosion. In this way the element formed from fire-proof material changes its shape or volume only slightly. The appears a compact and strong structure while the proportion of the carrier and swelling agent carefully selected ensure the shape of fire barrier to be kept. The components of the swelling agent have been chosen in such proportions that the swelling starts at the temperature of about 100 degrees centigrade, at the same time when the foamed polystyrene starts disappearing.

Principal use of the invention

The subject of the invention has been presented bellow in the examples of its realization.

Example I

- 5 94 per cent of foamed polystyrene granules by volume, with the granules of 0,5 up to 10 mm have been prepared. Separately, in the mixer, swelling agent has been prepared in the quantity of 6 per cent by volume.
- 10 The essential component of the swelling agent is sodium water-glass which constitutes a solution of technical sodium silicates with the formula $\text{Na}_2\text{O} \times \text{SiO}_2 \times n\text{H}_2\text{O}$, in the form of a transparent liquid with alkaline reaction, in the quantity of 75 per cent and the colloidal silica with bulk density of 60 g/dcm^3 , the density of $2,2 \text{ g/cm}^3$, specific surface of 300 up to $350 \text{ m}^2/\text{g}$ and with the diameter of the
- 15 particles of 15 up to 20 μ in the quantity of 22 per cent. The alkaline aqueous solution of sodium methylsiliconate was used in the quantity of 2 per cent as the hydrophobizer of the swelling agent. The task of the hydrophobizer is to
- 20 bind the water in the system of water glass with colloidal silica. Additionally, 0,5 per cent of sodium aluminosilicate has been introduced as the mineral pigment which is resistant to lyes as well as 0,7 per cent of zinc oxide as the hiding pigment.
- 25 All the components of the swelling agent in the above percentage were mixed in a mixer for about 15 minutes. As soon as the total homogeneity of the swelling agent is achieved, it is mixed with the previously prepared quantity of foamed polystyrene granules and through this mixing the
- 30 granules are being surrounded by the swelling agent. The fire resistant door made from metal sheet are filled with such a material. Under the influence of high temperature the swelling agent increases its dimensions and fills the empty space after the foamed polystyrene which starts
- 35 to disappear. The fire-proof material creates a compact

structure with high mechanical resistance. The fire -stopping door, depending on the thickness of fire-proof material filling the door, has an increasing fire-resistance.

Example II

5 85 per cent of ground foamed polystyrene by volume with the granules of 0,5 up to 20 mm have been prepared. Separately, in the mixer, 15 per cent of the swelling agent have been prepared. The swelling agent consist of 84 per cent of water glass /potassium/, 8 per cent of colloidal
10 silica, 5 per cent of alkaline solution of sodium methylsiliconate as a hydrophobizer, 1,6 per cent of sodium aluminosilica as a pigment, 1,4 per cent of zinc oxide as a hiding pigment.

After the full homogenization of the swelling agent it is
15 mixed with the foamed polystyrene ground previously and as soon as the foamed polystyrene is surrounded by the swelling agent, plates with 47 mm thickness have been produced from the material in the coatings from metal sheet. A fire stop has been made from these plates, which was tested
20 in the temperature increasing up to 1100 degrees centigrade. The plates showed fire-resistance amounting 65 minutes.

Industrial application

25 The fire-proof material, according to this invention, can be used at the construction of light fire-walls, for filling the fire-resistant doors, construction of fire dams and fire stopping walls in mining engineering, for filling of internal space of the constructions with special fire-resistance, and also for filling the empty space in the
30 cars, and this filling is light and fully non-flamable. The small weight of fire-proof material allows to decrease the weight e.g. of fire resistant doors in comparison with fire-proof doors known so far and in the same way to decrease

se the dimensions, weight and resistance of furniture, hinges etc. and to decrease the weight of the door frames, what is of great importance at construction of huge fire-resistant gates.

5 In normal conditions, i.e. without high temperature, the fire-proof materials according to this invention shows a high heat insulation power allowing to use it in the doors of cold stores.

10 This fire-proof material has no limitation in housing and at the construction of public buildings as far as the contact with food or living organism is concerned. It can be used everywhere because it is non toxic.

Patent claim

The fire-proof material consisting of the carrier and the agent increasing its volume under the influence of temperature, having water-glass as its component is characterized by the fact that the most advantageous carrier are
5 the granules of foamed polystyrene with the granules of 0,5 up to 20 mm in the quantity of 85 to 94 per cent by volume, surrounded by the swelling agent in the quantity of 6 to 15 per cent by volume, consisting of water-glass in the quantity of 65 to 85 per cent, advantageously co-
10 lloidal silica in the quantity of 2 to 35 per cent, hydrophobizer in the quantity of 0,5 to 5 per cent and the colouring mineral pigment in the quantity of 0,1 to 1,8 per cent and hiding mineral pigment in the quantity of 0,2 to 2 per cent.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/PL 92/00002

I. CLASSIFICATION F SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 C09K21/14; E04C2/20		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	C09K ; E04C	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	WORLD PATENTS INDEX LATEST Derwent Publications Ltd., London, GB; AN 82-85172E & SU,A,885 234 (SIBORGGAZSTROI) 30 November 1981 see abstract	1
X	WORLD PATENTS INDEX LATEST Derwent Publications Ltd., London, GB; AN 86-158733 & JP,A,61 091 049 (SHIMIZU) 8 October 1984 see abstract	1
X	WORLD PATENTS INDEX Derwent Publications Ltd., London, GB; AN 80-59669C & JP,A,55 091 658 (GIJUTSU) 12 July 1980 see abstract	1
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IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
06 MARCH 1992	17. 03. 92	
International Searching Authority EUROPEAN PATENT OFFICE	Signature of Authorized Officer NICOLAS H. J. F.	

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
X	<p>WORLD PATENTS INDEX Derwent Publications Ltd., London, GB; AN 75-38272W & JP,A,49 103 919 (MOCHIDA) 30 August 1974 see abstract</p> <p>---</p>	1
X	<p>WORLD PATENTS INDEX Derwent Publications Ltd., London, GB; AN 79-051998 & JP,A,53 140 822 (ISHIKAWA) 8 December 1978 see abstract</p> <p>---</p>	1
A	<p>US,A,4 172 744 (ISHIKAWA) 30 October 1979 see abstract; claims 1,4</p> <p>---</p>	1
A	<p>DE,A,3 728 397 (BAYER AG) 9 March 1989 see claims 1,4,5</p> <p>---</p>	1
A	<p>DE,A,2 627 504 (STUERMAN & KESSLER) 29 December 1977 see the whole document</p> <p>---</p>	1

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. PL 9200002
SA 56119**

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-4172744	30-10-79	JP-C- 1285351	09-10-85
		JP-A- 51116874	14-10-76
		JP-B- 60004235	02-02-85
		AT-B- 358827	10-10-80
		AT-B- 358828	10-10-80
		AT-B- 359289	27-10-80
		AU-B- 503793	20-09-79
		BE-A- 839203	01-07-76
		CA-A- 1075096	08-04-80
		CH-A- 625826	15-10-81
		DE-A, B, C 2609214	20-01-77
		FR-A, B 2315489	21-01-77
		GB-A- 1544450	19-04-79
		NL-A- 7602295	28-12-76
		SE-A- 7603014	25-12-76
		SE-A- 7907937	25-09-79
		US-A- 4107376	15-08-78

DE-A-3728397	09-03-89	None	

DE-A-2627504	29-12-77	None	
